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### Catalytic cracking and hydrotreating process for producing gasoline from hydrocarbon feedstocks containing sulfur

The present invention relates to a catalytic cracking and hydrotreating process for gasoline production from sulfur-containing hydrocarbon feedstocks.

Cracking processes, both thermal and catalytic, have constituted the heart of petroleum refining operations for several decades. The purpose of both types of process is the same, i.e., to break heavy molecular feed components into lower boiling, more valuable components. The thermal process, which has now been largely replaced by the more effective catalytic process, accomplishes this result by heat, whereas the catalytic process breaks the large molecules by contact between a heavy feed and an active catalyst at lower temperatures than used in thermal processes. The reactions which occur in the catalytic cracking operation are complex including, not only carbon-carbon bond scission but isomerization, alkylation, dehydrogenation, etc., and a carbonaceous material, or coke, is inevitably deposited on the catalyst. The catalyst, in such unit, is regenerated in a separate vessel, i.e., a regenerator, by burning off the coke to restore its activity. Commonly, the catalyst is continuously cycled between the reactor and regenerator as a moving bed without shutdown of either unit.

The economics of the catalytic cracking unit in a refinery, because of its high degree of flexibility, to a large extent, determines the product slate which will be produced by a refinery. Products from the catalytic cracking unit thus provide feed for other units, e.g., alkylation and polymerization units. Cat cycle stocks are used to make lubes, and gas is employed as fuel in the refinery. However, a major portion of the product of the catalytic cracking units of a given refinery are blended directly in gasoline blending pools which serve as supplies of motor gasoline. With the phaseout of lead anti-knock compounds it continues a formidable challenge for the refiner to maintain gasoline pools at the octane levels demanded; and, the problem is aggravated by the depletion of conventional petroleum supplies which creates an increased need to process heavy feedstocks such as residual, unconventional heavy crudes and the like for conversion to gasoline.

Cat cracking feed stocks are provided by atmospheric and vacuum stills, phenol extraction plants and hydrotreaters. The usual feed to a commercial catalytic cracking unit is comprised of a gas oil boiling below about 565.6°C (565.6°C—) (1050°F (1050°F—)), typically a virgin gas oil boiling between about 315.6°C (600°F) and 565.6°C (1050°F). In addition, thermally cracked materials are often used as cat cracking feeds. While various conventional types of processing, e.g., cat naphtha reforming and cat naphtha extraction, might be employed to upgrade cat naphtha octanes and increase the supply of high octane gasoline in the gasoline pool as lead is phased out of gasoline, most are quite expensive; particularly cat naphtha reforming which requires initial hydrotreating of the feed so that it can meet reformer feed specifications.

The bulk of the sulfur in a gasoline blending pool is contributed by cat naphtha, or product of the cat cracking units. The addition of large amounts of sulfur to a gasoline blending pool raises acute problems, particularly in view of the present requirements in many countries to meet emission standards for hydrocarbons (HC) and carbon monoxide (CO). Thus automobiles are now equipped with catalytic converters for the purpose of lowering emissions of CO and HC, but the new standards will also impose restrictions on NO<sub>x</sub> emissions, as well as added restrictions of CO and HC emissions. Sulfur, however, is a known poison for the more useful, and active "three-way" catalysts contemplated by the auto industry for use in catalytic converters to meet the 1980's standards. Consequently, the activity and activity-maintenance of the catalysts are suppressed due to the presence of sulfur. Moreover, it has been found that, due to the presence of the sulfur, the catalytic converters emit sulfate, either as a sulfuric acid aerosol or as particulates caused by sulfuric acid corrosion of the metal portions of the exhaust train. The sulfur in gasoline, which is typically present in amounts of about 300 ppm, is oxidized in the combustion chamber of the engine to sulfur dioxide. The catalytic converter, which is required for lowering the emissions of CO and HC, is thus responsible for the oxidation of sulfur dioxide in the exhaust gas to produce sulfur trioxide which immediately hydrates due to the presence of water vapor, one of the combustion products, to form a sulfuric acid aerosol or acid particulates, neither of which is environmentally acceptable.

Whereas cat naphtha hydrofining might be employed to produce low sulfur gasoline or a naphtha which can meet reformer feed specifications such treatment would be very expensive for such processes would require considerable hydrogen consumption, and hydrogen is a rather expensive commodity. Hydrogen constitutes a major cost in hydrotreating a cat naphtha because typically from about 20 to 40 percent and perhaps 60 percent and higher of the feed is olefinic, and a considerable amount of hydrogen is required for saturation of the olefins. The olefins must be virtually completely saturated before the cat naphthas can be reformed over a platinum or promoted platinum catalyst, this requiring generally from about 35.62 to 71.25 litres of hydrogen/litre of feed (200 to 400 SCF of hydrogen/B. of feed) to saturate the olefins typically contained in an intermediate boiling range cat naphtha. Moreover, in addition to the restrictive olefins specifications imposed on a cat naphtha feed, such feed also contains considerable amounts of sulfur and nitrogen, and far more severe hydrotreating of the cat naphtha to bring it in line with sulfur and nitrogen reformer feed specifications is required than even is necessary in hydrotreating virgin naphtha. In fact, in cat naphtha hydrofining mercaptan

reversion reactions, or reactions wherein the hydrogen sulfide by-product reacts with cat naphtha olefins to form mercaptans is a troublesome problem; for mercaptans cannot be tolerated in significant amounts within the feed, mercaptans must thus be eliminated by hydrofining, or hydrotreating the cat naphtha at severe conditions.

- 5 While the degree of olefins saturation with resultant octane loss can be diminished by proper selection of hydrotreating operating variables, and catalyst type, refiners cannot tolerate even small reductions in cat naphtha octane ratings, particularly now when lead is being phased out of gasoline blending pools; much less the loss in naphtha octane ratings caused by further increased olefin saturation resultant from the high severities which now appear necessary in order to lower gasoline  
10 sulfur limits within the ranges required.

It is the primary objective of the present invention to provide an improved process which will at least in part overcome these and other disadvantages of present catalytic cracking processes, and in fact provide a new and novel multiple stage catalytic cracking process for the cracking of gas oils.

- It is already known from US—A—3759821 to upgrade catalytically cracked gasoline by a  
15 process comprising fractionating said catalytically cracked gasoline into two fractions which are  $C_{6-}$  and  $C_{7+}$  fractions, contacting the  $C_{7+}$  fraction under conversion conditions with a crystalline aluminosilicate zeolite, preferably of type ZSM-5 or ZSM-8, and blending the liquid product obtained from the conversion with said  $C_{6-}$  fraction to obtain a gasoline having an enhanced octane number.

- US—A—3950242 describes and claims a method for producing a gasoline boiling range product  
20 which comprises cracking a petroleum fraction boiling from about 400°F (204.4°C) to 1100°F (593.3°C) in the presence of a crystalline zeolite cracking catalyst under conditions of temperature, pressure, space velocity and catalyst to oil ratio providing a conversion level of at least 45 vol.% of said fraction to produce a material having a 90% ASTM boiling point of 400°F (204.4°C) and comprising not more than 15 wt.% olefins in the depentanised gasoline product thereof, and contacting the  
25 depentanised gasoline of restricted olefin content with a ZSM-5 type crystalline zeolite conversion catalyst at a temperature within the range of 500 to 800°F (260.0 to 426.7°C) to produce a higher octane product.

The present invention provides a process for the production of high octane gasoline comprising the following steps in combination:

- 30 (a) cracking a hydrocarbon feed in a first cracking zone over a first cracking catalyst to obtain a cat cracked naphtha product;  
(b) withdrawing the cat cracked naphtha product from the first cracking zone;  
(c) re cracking said cat cracked naphtha product or one or more fractions thereof, without dilution with other hydrocarbons, over a crystalline aluminosilicate zeolite catalyst in a second cracking zone  
35 to saturate at least some of the olefin content thereof, characterised in that the hydrocarbon feed is a sulfur-bearing hydrocarbon feed and the cat cracking of step (a) results in a cat cracked naphtha product having an olefin content in the range of from 10 to 60%, based on the weight of the said naphtha product, and in step (c), the naphtha product or at least one fraction thereof is desulfurized and at least 50% of the olefins, based on the weight of the cat cracked naphtha product or fraction thereof,  
40 are saturated, and the process further comprises step (d) in which at least a fraction of the re cracked product of step (c) is hydrotreated or hydrofined to produce a high octane gasoline or gasoline blending component of low sulfur content.

- Thus the present invention provides a process having as an essential feature the step of re cracking a cracked naphtha feed containing up to 60 percent, suitably from 20 to 40 percent olefins  
45 over a crystalline aluminosilicate zeolite catalyst to further crack the naphtha and saturate at least 50 percent of the olefins, preferably from 80 percent to 100 percent of the olefins, based on the weight of said cracked naphtha feed. Suitably, the cracked naphtha feed is contacted and reacted over the catalyst, without dilution of said feed, at a temperature ranging from 426.7 to 593.3°C (800°F to 1100°F), preferably from 482.2 to 554.4°C (900°F to 1030°F), and at a gauge pressure ranging from  
50 0 to 344.75 kPa (0 to 50 pounds per square inch gauge (psig)), preferably from 43.475 to 137.9 kPa (5 psig to 20 psig). Reaction at such conditions not only produces significant saturation of the olefins, but also significant hydrodenitrogenation and hydrodesulfurization of said cat naphtha feed.

- In its preferred aspects the process is one wherein a conventional sulfur-bearing cat cracker feed, suitably a gas oil, is catalytically cracked, at conventional conditions, in an initial or first stage to  
55 provide a cat naphtha product containing generally from 10 to 60 percent, preferably from 20 to 40 percent olefins. The cat naphtha product in whole or in part is then re cracked, as an undiluted feed, in a subsequent or second catalytic cracking zone over a crystalline aluminosilicate zeolite catalyst. Preferably, the cat naphtha product of the initial or first stage is split into fractions inclusive of a low octane, highly olefinic intermediate fraction having a low end boiling point ranging from 48.9 to  
60 121.1°C (120°F to 250°F), preferably from 82.2 to 104.4°C (180°F to about 220°F), and a high end boiling point ranging from 121.1 to 193.3°C (250°F to about 380°F), preferably from 132.2°C to 176.7°C (270°F to 350°F). A higher boiling fraction having a low end boiling point range from 121.1 to 193.3°C (250°F to 380°F), preferably from 132.2 to 176.7°C (270°F to 350°F), and a higher end boiling point range from 176.7°C to 232.2°C (350°F to 450°F), preferably from 204.4 to 221.1°C  
65 (400°F to 430°F) can also be obtained. The intermediate or higher boiling fraction, or a composition

which includes both, may be utilized as feed and further catalytically cracked, or re-cracked, in a subsequent stage over a crystalline aluminosilicate zeolite catalyst sufficient to produce significant saturation of the olefins, and hydrodenitrogenation and hydrodesulfurization of said cat cracked naphtha fraction, or fractions. The re-cracked product is then hydrotreated, or hydrofined, at mild hydrotreating conditions to provide a low sulfur gasoline of improved octane.

Alternatively, the higher boiling fraction or fraction typically having a low end boiling point ranging from 121.1 to 193.3°C (250°F to 380°F) and a high end boiling point ranging from 176.7 to 232.2°C (350°F to 450°F) is not re-cracked because it is generally of relatively high octane and upgrading of this fraction is not required. The intermediate fraction per se, preferably, is utilized as a feed and further catalytically cracked, or re-cracked, in a subsequent stage over a crystalline aluminosilicate zeolite catalyst sufficient to produce significant saturation of the olefins, and hydrodenitrogenation and hydrodesulfurization of said cat cracked naphtha fraction. The re-cracked product thereof, is then hydrotreated, or hydrofined, at mild hydrotreating conditions, and then reformed over a conventional catalyst at conventional reforming (hydroforming) conditions to provide a low olefin gasoline of improved octane.

It has been found, quite surprisingly, that the re-cracking of an undiluted cracked naphtha, notably the intermediate of high boiling fractions, over a zeolite catalyst at rather low or mild conditions significantly increases the octane number while reducing the olefin content of the cracked naphtha by saturation of the olefins, without direct hydrogen addition. This reduction of olefin content while increasing octane number is indeed surprising. This re-cracking not only virtually eliminates any necessity of hydrotreating the cracked naphtha to reduce its olefin content, but also significantly reduces the nitrogen and sulfur content of the cracked naphtha. In particular, it has been found that re-cracking reduces the sulfur content of the feed by up to about 75 percent, or higher, based on the weight of the sulfur in the cat cracked naphtha. Thereafter, only a mild hydrotreatment of the cat cracked naphtha product is required to eliminate residual sulfur and thereby render the product susceptible to reforming, if desired, over highly sulfur-sensitive catalysts to further improve the octane number. This, of course, significantly reduces the capital cost of the required hydrotreater (or hydrofiner) and direct high costs of hydrotreating a cracked naphtha to reforming feed specifications. Furthermore, re-cracking of the cracked naphtha in this manner prior to hydrotreatment of the cracked naphtha to eliminate olefins minimizes mercaptan reversion reactions wherein olefins normally react with by-product hydrogen sulfide to form mercaptans, any significant amount of which simply cannot be tolerated in a reformer feed.

Various cracking catalysts can be used in cracking the gas oil feed, or feed to the first stage catalytic cracker. Suitable cracking catalysts include conventional silica-based materials. Exemplary of such catalysts are, e.g. amorphous silica-alumina; silica-magnesia; silica-zirconia; conventional clay cracking catalysts, and the like. The amorphous gel silica-metal oxide cracking catalyst may further be composited with kaolin in amounts of 10 to 40 wt.% (based on total weight of the composited catalyst) and up to 20 wt.% or more crystalline aluminosilicate zeolite, such as faujasite. A crystalline aluminosilicate zeolite catalyst is required in the second stage catalytic cracker, i.e., for cracking the cat cracked naphtha, or fraction thereof, from the first stage. These catalysts are well known and commercially available. Preferably, the catalyst utilized, particularly in the second stage catalytic cracker is an amorphous silica-alumina catalyst containing from 5 to 16 weight percent  $\gamma$ -type faujasite, and, optionally 15 to 40 percent kaolin.

Generally, the first and second stage catalytic crackers are operated at about the same absolute conditions of temperature, pressure, space velocity, and catalyst/oil ratio, the runs being initiated by adjusting the feed and catalyst rates, and the temperature and pressure of the reactor to operating conditions. The catalytic cracking operation in both stages of cracking is continued at conditions by adjustment of the major process variables, within the ranges described below:

| Major operating variables             | Typical process conditions | Preferred process conditions |
|---------------------------------------|----------------------------|------------------------------|
| Pressure, (Psig) kPa gauge            | (0—50) 0 to 344.75         | (5—20) 34.475 to 137.9       |
| Reactor temp., (°F)°C                 | (800—1100) 426.7 to 593.3  | (900—1030) 482.2 to 554.4    |
| Space velocity, W/W/Hr                | 2—200                      | 5—150                        |
| Catalyst/oil ratio,                   | 2—12                       | 4—8                          |
| (instantaneous vol. of reactor space) |                            |                              |
| kgs/per kg of oil                     |                            |                              |

The product of the first stage catalytic cracker, suitably a cat cracked naphtha obtained by cracking a gas oil, is characterized as a cracked naphtha having an olefin content ranging from 10 percent to 60 percent, more typically from 20 percent to 40 percent (by weight) and boiling within the gasoline range, typically from 18.3°C (65°F) to 221.1°C (430°F) (i.e.,  $C_6$  to 221.1°C,  $C_9$ /430°F). All or a portion of the cat cracked naphtha, preferably an intermediate or heavy fraction, or composition

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which includes both fractions, as previously defined, is split from the product of said first stage, fed into, and cracked, without dilution, over the crystalline aluminosilicate zeolite catalyst in the second stage catalytic cracker. The cracked product is then subjected to a mild hydrotreatment by contact, with a catalyst comprising a composite of an inorganic oxide base, suitably alumina, and a Group VI—B or Group VIII metal, or both, e.g., a cobalt molybdenum ("moly")/alumina catalyst, at conditions given as follows, to provide a gasoline suitable for addition to a gasoline blending pool, to wit:

| Process variable                     | Typical process conditions | Preferred process conditions |
|--------------------------------------|----------------------------|------------------------------|
| Pressure, (psig) kPa gauge           | (60—500) 413.7 to 3447.5   | (80—200) 551.6 to 1379       |
| Temperature, (°F)°C                  | (400—800) 204.4 to 426.7   | (500—600) 260.0 to 315.6     |
| Feed rate, LHSV (h <sup>-1</sup> )   | 1—80                       | 5—20                         |
| Hydrogen rate, (SCF/Bbl) l/l naphtha | (200—4000) 35.62 to 712.5  | (800—2000) 142.5 to 356.2    |

Alternatively, the cracked product is subjected to the following mild hydrotreating conditions so as to provide a naphtha suitable as a feed to a reforming process:

| Process variable                     | Typical process conditions  | Preferred process conditions |
|--------------------------------------|-----------------------------|------------------------------|
| Pressure, (psig) kPa gauge           | (100—2000) 689.5 to 13790.0 | (200—300) 1379.0 to 2068.5   |
| Temperature, (°F)°C                  | (400—800) 204.4 to 426.7    | (500—600) 260.0 to 315.6     |
| Feed rate, LHSV (h <sup>-1</sup> )   | 1—25                        | 2—6                          |
| Hydrogen rate, (SCF/Bbl) l/l naphtha | (200—3000) 35.62 to 534.3   | (200—500) 35.62 to 89.06     |

The product from the hydrofiner is subjected to reforming, at reforming conditions, by contact with a sulfur-sensitive, noble metal reforming catalyst to produce a satisfactory high octane gasoline. Suitably, the reforming run is initiated by injection of hydrogen into the reforming reactor (or zone) with the feed at the desired hydrogen and feed rates, with adjustment of the temperature and pressure to operating conditions. The run is continued at optimum reforming conditions by adjustment of the major process variables, within the ranges described below:

| Major operating variables                         | Typical process conditions  | Preferred process conditions |
|---|-----------------------------|------------------------------|
| Pressure, (Psig) kPa gauge                        | (50—750) 344.75 to 5171.25  | (100—300) 689.5 to 2068.5    |
| Reactor temp., (°F)°C                             | (750—1100) 398.9 to 593.3   | (850—1000) 454.4 to 537.8    |
| Gas rate, (SCF/B) l/l naphtha (incl. recycle gas) | (1500—10,000) 267.2 to 1781 | (2000—7000) 356.2 to 1247    |
| Feed rate, W/W/Hr                                 | 0.5—10                      | 1—3                          |

The catalyst employed in reforming is one comprising a refractory or inorganic oxide support material, particularly alumina, which is composited with a Group VIII noble metal hydrogenation-dehydrogenation component, notably platinum, to which may be added an additional metal, or metals, to promote the activity and selectivity of the catalysts, particularly iridium or rhenium, or both, or component selected from the Group IV metals, Group VI metals, Group VII metals, and Group VIII metals, e.g., germanium, tin, lead, osmium, ruthenium, rhodium or the like. A halogen component, suitably chlorine, is generally added to provide the desired acidity. These components can be added to a support by any of the conventional methods, e.g., by impregnation prior to, following or simultaneously with the impregnation of the noble metal, or halogen components. The metal hydrogenation-dehydrogenation components, or promoters are added to a support in concentration ranging about 0.01 to 3 percent, preferably from about 0.05 to about 1 percent, based on the weight of the catalyst. A suitable support can contain, e.g., one or more of alumina, bentonite, clay, diatomaceous earth, zeolite, silica, activated carbon, magnesia, zirconia, thorina, and the like; though the most preferred support is alumina to which, if desired, can be added a suitable amount of other refractory carrier materials such as silica, zirconia, magnesia, titania, etc., usually in a range of about 1 to 20 percent, based on the weight of the support. A preferred support is one having a surface area of more than 50 m<sup>2</sup>/g, preferably from 100 to 300 m<sup>2</sup>/g, a bulk density of 0.3 to 1.0 g/ml, preferably 0.4 to 0.8 g/ml, an average pore volume of 0.2 to 1.1 ml/g, preferably 0.3 to 0.8 ml/g, and an average pore diameter of 30 to 300Å (3 to 30 nm).

The invention will be more fully understood by reference to the following nonlimiting

demonstrations and examples which, present comparative data which illustrate its more salient features. All parts are given in terms of weight unless otherwise specified.

In a first step, a 68.3/211.7°C (155°F/413°F) cat naphtha fraction was obtained by catalytically cracking a virgin gas oil at conventional conditions over a conventional catalyst to obtain a cat cracked naphtha, hereinafter referred to as Feedstock A, the complete feedstock inspections of which are given in Table I, below.

TABLE I

| Feedstock A                            |                |         |             |
|--|----------------|---------|-------------|
| 68.3/211.7°C (155°F/413°F) cat naphtha |                |         |             |
|  | Sulfur, wppm   | 572     |             |
|  | Nitrogen, wppm | 30      |             |
|  | Br. no., cc/gm | 24.8    |             |
| Octane                                 |                |         |             |
|  | RONC           | 82.8    |             |
|  | MONC           | 75.2    |             |
| FIA, vol. %                            |                |         |             |
|  | Arom.          | 33.6    |             |
|  | Olefins        | 15.3    |             |
|  | Saturates      | 51.0    |             |
| ASTM D-86                              |                | °F      | °C          |
|  | IBP/5%         | 155/194 | 68.3/90.0   |
|  | 10/20          | 207/228 | 97.2/108.9  |
|  | 30/40          | 245/262 | 118.3/127.8 |
|  | 50/60          | 280/300 | 137.8/148.9 |
|  | 70/80          | 320/337 | 160.0/169.4 |
|  | 90/95          | 365/383 | 185.0/195.0 |
|  | FBP            | 413     | 211.7       |

## Example 1

Feedstock A was hydrofined in a reactor at 287.8°C (550°F), 2758 kPa gauge (400 psig), and 142.5 litres H<sub>2</sub>/litre feedstock (800 SCF/B) over a cobalt moly-on-alumina catalyst to produce a low sulfur gasoline blending component having a Bromine number of about 5 and 20 wppm sulfur, this requiring about 96.5% hydrosulfurization. The product has a research octane number (RONC) at 77.3 and a motor octane number (MONC) of 73.0, this representing a loss of 5.5 RONC and a 2.2 loss of MONC as a result of the hydrofining.

## Example 2

Feedstock A was re-cracked in a reactor at 498.9°C (930°F), 101.36 kPa absolute (14.7 psia), 13.7 WHSV and at a catalyst/oil ratio of 9.2 over a conventional commercial zeolite cracking catalyst containing crystalline aluminosilicate zeolite, silica alumina gel and clays, and the product then fractionated to provide a light ends cut, and three fractions, i.e., a low boiling 18.3/93.3°C (65/200°F) fraction, an intermediate 93.3/221.1°C (200/430°F) fraction and a high boiling 221.1°C+ (430°F+) fraction, the low boiling and intermediate boiling fractions being characterized in Table II.

TABLE II

|        |                | 18.3/93.3°C<br>(65/200°F) | 93.3/221.1°C<br>(200/430°F) |
|--------|----------------|---------------------------|-----------------------------|
|        | Vol. % on feed | 24.9                      | 55.9                        |
|        | Sulfur, wppm   | 42                        | 244                         |
|        | Br. no.        | 20.0                      | 3.0                         |
| Octane |                |                           |                             |
|        | RONC           | 85.0                      | 90.4                        |
|        | MONC           | 80.0                      | 80.9                        |

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The 93.3/221.1°C (200/430°F) fraction is then hydrofined at 287.8°C (550°F), 2758 kPa gauge (400 psig), 142.5 litres H<sub>2</sub>/litre naphtha fraction (800 SCF/Bbl) over a cobalt moly-on-alumina catalyst as in Example 1 to produce a low sulfur gasoline blending component having Bromine No. of about 1 and containing 11 wppm sulfur, this requiring about 95.5% hydrodesulfurization. The resulting product has octane ratings of 89.4 RONC and 80.9 MONC. Thus, the loss in octane rating for this low sulfur gasoline blending component is nil as relates to the motor octane number rating, and only 1 octane number as relates to research octane number.

When the cracked 18.3/93.3°C (65/200°F) and 93.3/221.1°C (200/430°F) cracked, hydrofined fractions are combined, the resultant product has an octane number of 88.7 RONC and 80.6 MONC, contains only 20 wppm of sulfur, and represents 80.8 vol. percent recovered product, based on the original feed. Octane loss as a result of hydrofining is estimated at about 0.5 RONC, or less.

The following example demonstrates a more preferred embodiment wherein an intermediate fraction only is cracked.

## Example 3

Feedstock A was split into three fractions, a 18.3/93.3°C (65/200°F) fraction, a 93.3/165.6°C (200/330°F) fraction, and a 165.6°C+ (330°F+) fraction as defined in Table III.

TABLE III

|                |  | 18.3/93.3°C<br>(65/200°F) | 93.3/165.6°C<br>(200/330°F) | 165.6°C+<br>(330°F+) |
|----------------|--|---------------------------|-----------------------------|----------------------|
| Vol. % on feed |  | 17.2                      | 61.9                        | 20.9                 |
| Sulfur, wppm   |  | 100                       | 226                         | 1,841                |
| Br. no.        |  | 54.6                      | 24.6                        | 7.8                  |
| Octane         |  |                           |                             |                      |
| RONC           |  | 87.5                      | 81.6                        | 82.5                 |
| MONC           |  | 79.2                      | 75.3                        | 75.0                 |

The 18.3/93.3°C (65/200°F) fraction is then treated in a Merox\* process, after admixture with light ends from the 93.3/165.6°C (200/330°F) fraction which is cracked as defined hereafter, to produce a product of 87.5 RONC and 79.2 MONC with 50 ppm sulfur.

The 93.3/165.6°C (200/330°F) fraction is cracked in a reactor at 498.9°C (930°F), 101.36 kPa absolute (14.7 psia), 13.7 WHSV at a catalyst/oil ratio of 9.2 over a conventional commercial zeolite, silica-alumina gel and clays, and the product then fractionated to provide a 18.3/93.3°C (65/200°F) fraction which is blended with the 18.3/93.3°C (65/200°F) fraction to Merox, a 93.3/221.1°C (200/430°F) fraction, and a 221.1°C+ (430°F+) fraction. The 18.3/93.3°C (65/200°F) and 93.3/221.1°C (200/430°F) fractions are characterized in Table IV.

TABLE IV

|                |  | 18.3/93.3°C<br>(65/200°F) | 93.3/221.1°C<br>(200/430°F) |
|----------------|--|---------------------------|-----------------------------|
| Vol. % on feed |  | 10.7                      | 39.3                        |
| Sulfur, wppm   |  | 67                        | 88                          |
| Br. no.        |  | 20.4                      | 2.7                         |
| Octane         |  |                           |                             |
| RONC           |  | 87.3                      | 89.6                        |
| MONC           |  | 80.0                      | 80.2                        |

The 165.6°C+ (330°F+) fraction, characterized in Table III, is combined with the 93.3/221.1°C (200/430°F) and 221.1°C+ (430°F+) cracked fractions, then hydrofined over a cobalt moly-on-alumina catalyst at 287.8°C (550°F), 2758 kPa gauge (400 psig) and 142.5 litres H<sub>2</sub>/litre naphtha fractions (800 SCR/B). The feed entering the hydrofiner (H/F Feed), the product therefrom (H/F Product), and the final product formed by combining the hydrofined product and product from Merox\* is characterized in Table V.

\*"Merox" is a registered trade mark

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TABLE V

|    |                | H/F feed | H/F product | Final product |
|----|----------------|----------|-------------|---------------|
| 5  | Vol. % on feed | 60.2     |             | 88.1          |
|    | Sulfur, wppm   | 711      | 8.2         | 20            |
|    | Br. no.        | 4.5      | 1.1         |               |
|    | Octane         |          |             |               |
| 10 | RONC           | 88.5     | 87.5        | 87.5          |
|    | MONC           | 78.4     | 78.4        | 78.7          |

These data show that the octane loss due to hydrofining the final product is considerably improved as contrasted with hydrofining the original feed, and that octane loss as a result of the hydrofining approximates only 0.8 RON, with no loss in MON octane value. Naphtha yield is considerably improved with no greater octane loss due to hydrofining as contrasted with re cracking the whole naphtha.

## Example 4

Feedstock A was re cracked in a reactor at 498.9°C (930°F), 101.36 kPa absolute (14.7 psia), 13.7 WHSV and at a catalyst/oil ratio of 9.2 over a conventional commercial zeolite cracking catalyst containing crystalline aluminosilicate zeolite, silicate alumina gel and clays, and the product then fractionated to provide three fractions, i.e., a low boiling 18.3/93.3°C (65/200°F) fraction, an intermediate 93.3/176.7°C (200/350°F) fraction and a high boiling 176.7/221.1°C (350/430°F) fraction, as characterized in Table VI.

TABLE VI

|    |                | 18.3/93.3°C<br>(65/200°F) | 93.3/176.7°C<br>(200/350°F) | 176.7/221.1°C<br>(350/430°F) |
|----|----------------|---------------------------|-----------------------------|------------------------------|
| 30 | Vol. % on feed | 21.6                      | 48.6                        | 9.7                          |
|    | Sulfur, wppm   | 42                        | 91                          | 893                          |
|    | Nitrogen, wppm | 2                         | 2                           | 9.2                          |
|    | Br. no. cc/gm  | 20.3                      | 3.3                         | 1.41                         |
| 35 | Octane         |                           |                             |                              |
|    | RONC           | 85.1                      | 89.7                        | 93.8                         |
|    | MONC           | 80.0                      | 80.5                        | 82.9                         |
|    | FIA, vol. %    |                           |                             |                              |
| 40 | Arom.          | 3.8                       | 50                          | 74.7                         |
|    | Olefins        | 11.6                      | 0.6                         | 0.1                          |
|    | Saturates      | 84.6                      | 49.4                        | 25.1                         |

The 93.3/176.7°C (200/350°F) fraction is then hydrofined over a cobalt moly-on-alumina catalyst at conditions just sufficient to produce a suitable reforming feed, this requiring 98.9% hydrodesulfurization, 50% hydrodenitrogenation, and 70% saturation of the olefins to provide a product of 89 RONC with less than 1 ppm sulfur, less than 1 ppm nitrogen and a bromine number of less than 1. In forming this product a hydrogen consumption of 3.562 litres H<sub>2</sub>/litre feed (20 SCF/Bbl) is required.

The hydrofined fraction is then reformed over an iridium-promoted platinum catalyst at 498.9°C (930°F), 1.0 W/Hr/W, 1379 kPa gauge (200 psig) at a hydrogen to oil ratio of 855 litres/litre (4800 SCF/Bbl) to produce 100 RONC gasoline.

In sharp contrast, when Feedstock A was split into fractions without re cracking, the compositions given in Table VII were obtained, to wit:



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TABLE VII  
18.3/93.3°C 93.3/176.7°C 176.7/221.1°C  
(65/200°F) (200/350°F) (350/430°F)

|    |                |      |      |        |
|----|----------------|------|------|--------|
| 5  | Vol. % on feed | 17.2 | 61.9 | 18.9   |
|    | Sulfur, wppm   | 100  | 226  | 1084.8 |
|    | Nitrogen, wppm | 1.2  | 17.0 | 62.0   |
|    | Br. no. cc/gm  | 54.6 | 24.6 | 7.8    |
|    | Octane         |      |      |        |
| 10 | RONC           | 87.5 | 81.6 | 82.0   |
|    | MONC           | 79.2 | 75.3 | 75.1   |
|    | FIA, vol. %    |      |      |        |
| 15 | Arom.          | 4.7  | 39.4 | 59.2   |
|    | Olefins        | 33.1 | 8.4  | 5.7    |
|    | Saturates      | 62.2 | 52.2 | 35.1   |

These fractions are thus highly unsaturated as contrasted with similar fractions obtained by  
 20 re cracking Feedstock A, and contain considerably more sulfur and nitrogen. By way of further contrast,  
 however, a portion of the 93.3/176.7°C (200/350°F) fraction (Table VII) is then hydrofined over the  
 hydrofining catalyst previously defined at conditions just sufficient to achieve 99.6%  
 hydrodesulfurization, 94.1% hydrodenitrogenation and 96% saturation of the olefins to produce a  
 25 product suitable for reforming to 100 RONC, i.e., one which contained less than 1 ppm sulfur, less than  
 1 ppm nitrogen and a bromine number of less than 1. This produced a product of 75 RONC and  
 required over 26.72 litres H<sub>2</sub>/litre feed (150 SCF/Bbl of hydrogen), well over seven times the amount of  
 hydrogen required to hydrofine the re cracked product.

The re cracking of Feedstock A is thus shown to drastically reduce the amount of hydrotreating  
 required to produce a reformer feed, and it achieves this at far less severity and with far less  
 30 consumption of hydrogen. Moreover, assuming first order desulfurization kinetics, 20% less reactor  
 volume is required to achieve 98.8% hydrodesulfurization for the intermediate fraction of re cracked  
 Feedstock A than is required to produce 99.6% hydrodesulfurization for the intermediate fraction of  
 raw Feedstock A. It also reduces reforming severity, or the severity required to produce 100 RONC  
 gasoline.

35 The following example demonstrates a more preferred embodiment wherein an intermediate  
 fraction only is re cracked.

## Example 5

40 Another portion of the 93.3/176.7°C (200/350°F) fraction split from Feedstock A, as  
 characterized in Table VII, was re cracked at 498.9°C (930°F), 101.36 kPa absolute (14.7 psia), 14.3  
 WHSV and at a catalyst/oil ratio of 9.1. The product was then split into three fractions, a 18.3/93.3°C  
 (65/200°F) fraction, a 93.3/176.7°C (200/350°F) fraction, and a 176.7/221.1°C (350/430°F)  
 fraction as defined in Table VIII.

TABLE VIII  
18.3/93.3°C 93.3/176.7°C 176.7/221.1°C  
(65/200°F) (200/350°F) (350/430°F)

|    |                |      |      |      |
|----|----------------|------|------|------|
| 50 | Vol. % on feed | 17.3 | 60.8 | 2.7  |
|    | Sulfur, wppm   | 67   | 83   | 186  |
|    | Nitrogen, wppm | 1.0  | 3.0  | 17   |
|    | Br. no. cc/gm  | 20.4 | 2.7  | 3.5  |
|    | Octane         |      |      |      |
| 55 | RONC           | 87.4 | 89.6 | —    |
|    | MONC           | —    | 80.2 | —    |
|    | FIA, vol. %    |      |      |      |
| 60 | Arom.          | 0    | 45.4 | 97.5 |
|    | Olefins        | 10.2 | 2.6  | 1.0  |
|    | Saturates      | 89.8 | 52.1 | 1.5  |

The 93.3/176.7°C (200/350°F) fraction is then hydrofined over a cobalt moly-on-alumina  
 65 catalyst at conditions just sufficient to produce a suitable reforming feed, this requiring 98.8%  
 hydrodesulfurization, 67% hydrodenitrogenation, and 63% saturation of the olefins to provide a

product of 89.6 RONC with less than 1 ppm sulfur, less than 1 ppm nitrogen and a bromine number of less than one. In forming this product, a hydrogen consumption of 3.562 to 5.343 litres H<sub>2</sub>/litre oil (20 to 30 SCF/Bbl) is required.

The hydrofined fraction is then reformed over an Iridium promoted platinum catalyst at 498.9°C (930°F), 1.0 W/Hr/W, 1379 kPa (gauge (200 psig) at a hydrogen to oil ratio of 855 litres H<sub>2</sub>/litre oil (4800 SCB/Bbl) to produce 100 RONC gasoline.

These data thus show that re cracking the intermediate fraction of a cat naphtha offers definite advantages over re cracking the whole cat cracked naphtha. In comparing Example 5 with Example 4 it is thus shown that 85.6 percent of a C<sub>9</sub>/221.1°C (C<sub>9</sub>/430°F) product is obtained in re cracking an intermediate fraction vis-a-vis the 79.9 percent of C<sub>9</sub>/221.1°C (C<sub>9</sub>/430°F) product obtained in re cracking the whole of Feedstock A. Moreover, 60.8 percent of a 93.3/176.7°C (200/350°F) product is obtained in re cracking the intermediate fraction vis-a-vis the 48.6 percent of a 93.3/176.7°C (200/350°F) product obtained in re cracking the whole of Feedstock A. This fraction is particularly suitable as a reformer feed.

The preferred embodiment, as represented by Example 5, also provides higher selectivity for other relatively high value products vis-a-vis the embodiment of Example 4; or, conversely, lower selectivity for products of lesser value vis-a-vis the embodiment of Example 4. The data given in Table IX presents comparative data illustrative of the product of such relatively low value by-products as coke, light gases, inclusive of hydrogen and C<sub>1</sub> and C<sub>2</sub> hydrocarbons, and 221.1°C+ (430°F+) hydrocarbons, in the preceding runs wherein, as in Example 4, the whole of Feedstock A is re cracked, and in Example 5 an intermediate boiling feedstock is re cracked. The Table also presents the yields of C<sub>3</sub> and C<sub>4</sub> hydrocarbons which were obtained, these products being nearly as valuable as gasoline. The first column of Table IX identifies the by-product, the second column gives the percent yield of the by-product, based on the amount of re cracked feed which was treated, and the third column gives the percent yield, based on the amount of original Feedstock A.

TABLE IX

Yield, based on  
re cracked feedYield, based on  
feedstock A

| Product                   | Example 4 | Example 5 | Example 4 | Example 5 |
|---------------------------|-----------|-----------|-----------|-----------|
| Coke, wt. %               | 1.31      | 0.86      | 1.31      | 0.53      |
| Hydrogen, wt. %           | 0.0073    | 0.0067    | 0.0073    | 0.0041    |
| C <sub>1</sub> , wt. %    | 0.13      | 0.10      | 0.13      | 0.062     |
| C <sub>2</sub> , wt. %    | 0.70      | 0.53      | 0.70      | 0.33      |
| C <sub>3</sub> , wt. %    | 5.10      | 4.87      | 5.1       | 3.01      |
| C <sub>4</sub> , vol. %   | 11.00     | 13.4      | 11.0      | 8.3       |
| 221.1°C+ (430°F+), vol. % | 3.5       | 1.9       | 3.5       | 1.2       |

The advantages of re cracking an intermediate cut vis-a-vis a whole feed are apparent. In considering these data it is noted in particular that the 221.1°C+ (430°F+) product is of low API gravity, is not desirable for use as heating oil, and is unsuitable for use as diesel fuel or jet fuel. Only small levels of this 221.1°C+ (430°F+) product can be tolerated in gasoline for it contains multi-ring aromatics which cause serious engine deposits.

Table X presents data which illustrates that the preferred embodiment produces higher yields of the C<sub>3</sub> and C<sub>4</sub> hydrocarbons, which material is a potentially valuable alkylate feed. Analysis of the C<sub>3</sub> and C<sub>4</sub> hydrocarbons thus shows the following yield of C<sub>3</sub> and C<sub>4</sub> (and i-C<sub>4</sub>) hydrocarbons, based on re cracked feed.

TABLE X

Yield, based on re cracked feed

| Product                   | Example 4 | Example 5 |
|---------------------------|-----------|-----------|
| C <sub>3</sub> , wt. %    | 3.90      | 3.6       |
| C <sub>4</sub> , vol. %   | 3.61      | 4.54      |
| i-C <sub>4</sub> , vol. % | 6.21      | 7.24      |

The advantages of re cracking an intermediate boiling feed are therefore demonstrated. However, the re cracking of a heavier fraction, e.g., a 93.3 to 221.1°C (200/430°F) fraction, is preferable to re cracking a whole fraction, i.e., the 18.3 to 221.1°C (65/430°F) fraction for obviously, inter alia, the cracking of a 18.3 to 93.3°C (65/200°F) fraction will produce little 93.3 to 176.7°C (200/350°F) product for reforming, if any.

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It is apparent that various modifications and changes can be made without departing the spirit and scope of the invention.

### Conversion of units

- 5     Temperatures expressed in °F are converted to °C by subtracting 32 and dividing by 1.8.  
       Gas Volumes in Standard Cubic Feet (SCF) are converted to litres by multiplying by 28.32.  
       Liquid Volumes in Barrels (B or Bbl) are converted to litres by multiplying by 159.0.  
       Mass in pounds (lbs) is converted to kilograms by dividing by 2.20462.  
       Pressures in pounds per square inch (psi) are converted to kPa by multiplying by 6.895.  
 10    Pressures in pounds per square inch (psi) are converted to kg/cm<sup>2</sup> by multiplying by 0.07031.  
       Note "psia" denotes absolute pressure in psi and "psig" denotes gauge pressure in psi.

### Claims

- 15     1. A process for the production of high octane gasoline comprising the following steps in combination:  
       (a) cracking a hydrocarbon feed in a first cracking zone over a first cracking catalyst to obtain a cat cracked naphtha product;  
       (b) withdrawing the cat cracked naphtha product from the first cracking zone;  
 20     (c) cracking said cat cracked naphtha product or one or more fractions thereof, without dilution with other hydrocarbons, over a crystalline aluminosilicate zeolite catalyst in a second cracking zone to saturate at least some of the olefin content thereof, characterised in that the hydrocarbon feed is a sulfur-bearing hydrocarbon feed and the cat cracking of step (a) results in a cat cracked naphtha product having an olefin content in the range of from 10 to 60%, based on the weight of the said  
 25     naphtha product, and in step (c), the naphtha product or at least one fraction thereof is desulfurized and at least 50% of the olefins, based on the weight of the cat cracked naphtha product or fraction thereof, are saturated, and the process further comprises step (d) in which at least a fraction of the cracked product of step (c) is hydrotreated or hydrofined to produce a high octane gasoline or gasoline blending component of low sulfur content.  
 30     2. A process according to claim 1 characterized in that at least one of the said fractions of said cat cracked naphtha product comprises an intermediate fraction having a low end boiling point in the range of from 120°F (48.9°C) to 250°F (121.1°C) and a high end boiling point in the range of from 250°F (121.1°C) to 380°F (193.3°C).  
       3. A process according to claim 1 characterized in that at least one of said fractions of said cat  
 35     cracked naphtha product comprises a fraction having a low end boiling point in the range of from 180°F (82.2°C) to 220°F (104.4°C) and a high end boiling point in the range of from 400°F (204.4°C) to 430°F (221.1°C).  
       4. A process according to claim 2 characterized in that at least another fraction of said cat cracked naphtha product has a low end boiling point in the range of from 250°F (121.1°C) to 380°F  
 40     (193.3°C) and a higher end boiling point in the range of from 350°F (176.7°C) to 450°F (232.2°C).  
       5. A process according to claim 2 characterized in that a fraction of said cat cracked naphtha product having a low end boiling point in the range of from 250°F (121.1°C) to 380°F (193.3°C) and a higher end boiling point in the range of from 350°F (176.7°C) to 450°F (232.2°C) is not cracked in step (c).  
 45     6. A process as in any one of claims 2 to 5 characterised by comprising the additional step of reforming the product obtained from step (d).  
       7. A process as in any one of claims 1 to 6 characterised in that the olefin content of the cracked naphtha product is in the range of from 20 to 40 wt. % based on the weight of naphtha product.  
       8. A process according to any one of claims 1 to 7 characterised in that the said hydrotreating or  
 50     hydrofining conditions of step (d) are selected to result in a product suitable for addition to a gasoline blending pool, within the following ranges:

|    | Process variable                            | Process conditions           |
|----|---|------------------------------|
| 55 | Pressure kPa gauge (psig)                   | 413.7 to 3447.5 (60 to 500)  |
|    | Temperature, °C (°F)                        | 204.4 to 426.7 (400 to 800)  |
|    | Feed rate, LHSV (h <sup>-1</sup> )          | 1 to 80                      |
|    | Hydrogen/naphtha rate, litres/litre (SCF/B) | 35.62 to 712.5 (200 to 4000) |
| 60 |   |                              |

9. A process according to any one of claims 1 to 7 characterised in that the said hydrotreating or hydrofining conditions of step (d) are selected to result in a product suitable as a feed for reforming over a sulfur-sensitive noble metal reforming catalyst, within the following ranges:

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|   | Process variable                            | Process conditions           |
|---|---|------------------------------|
|   | Pressure, kPa gauge (psig)                  | 689.5 to 13790 (100 to 2000) |
|   | Temperature, °C (°F)                        | 204.4 to 426.7 (400 to 800)  |
| 5 | Feed rate, LHSV (h <sup>-1</sup> )          | 1 to 25                      |
|   | Hydrogen/naphtha rate, litres/litre (SCF/B) | 35.62 to 534.3 (200 to 3000) |

10. A process according to any one of claims 1 to 9 characterised in that the sulfur-bearing hydrocarbon feed introduced into said first cracking zone is a gas oil boiling below 1050°F (565.5°C).

11. A process according to any one of claims 1 to 10 characterised in that from 80 to 100 percent of the olefins of the cat cracked naphtha feed introduced into the second cracking zone are saturated during the reactions in the second cracking zone.

12. A process according to any one of claims 1 to 11 characterised in that the cat cracked naphtha feed introduced into the second cracking zone is reacted at a temperature in the range of from 800°F (426°C) to 1100°F (593.3°C) and at a pressure in the range of from 0 to 344.75 kPa gauge (0 to 50 psig).

13. A process according to any one of claims 1 to 12 characterised in that the cat cracked naphtha feed introduced into the second cracking zone is reacted at a temperature in the range of from 900°F (482.2°C) to 1030°F (554.4°C).

## Patentansprüche

1. Verfahren zur Herstellung von Benzin mit hoher Oktanzahl, bei dem
  - (a) ein Kohlenwasserstoffeinsatzprodukt in einer ersten Crackzone über einem ersten Crackkatalysator gecrackt wird, um ein katalytisch gecracktes Naphthaprodukt zu erhalten,
  - (b) das katalytisch gecrackte Naphthaprodukt aus der ersten Crackzone abgezogen wird und
  - (c) das katalytisch gecrackte Naphthaprodukt oder eine oder mehrere Fraktionen desselben ohne Verdünnung mit anderen Kohlenwasserstoffen über einem kristallinen Aluminiumsilikatzelolithkatalysator in einer zweiten Crackzone erneut gecrackt wird, um mindestens einen Teil des Olefingehaltes desselben abzusättigen, dadurch gekennzeichnet, daß das Kohlenwasserstoffeinsatzprodukt ein schwefelhaltiges Kohlenwasserstoffeinsatzprodukt ist, das katalytische Cracken in Stufe (a) zu einem katalytisch gecrackten Naphthaprodukt mit einem Olefingehalt im Bereich von 10 bis 60%, bezogen auf das Gewicht des Naphthaproduktes, führt, in Stufe (c) das Naphthaprodukt oder mindestens eine Fraktion desselben entschwefelt wird und mindestens 50% der Olefine, bezogen auf das Gewicht des katalytisch gecrackten Naphthaproduktes oder der Fraktion desselben, gesättigt werden und in der zusätzlichen Stufe (d) mindestens eine Fraktion des erneut gecrackten Produkts aus Stufe (c) einer Wasserstoffbehandlung unterworfen oder hydrofiniert wird, um ein Benzin oder eine Mischungskomponente für Benzin mit hoher Oktanzahl und geringem Schwefelgehalt zu erzeugen.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß mindestens eine der Fraktionen des katalytisch gecrackten Naphthaproduktes eine Zwischenfraktion mit einem unteren Siedepunkt im Bereich von 48,9 bis 121°C und einem oberen Siedepunkt im Bereich von 121,1°C bis 193,3°C enthält.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß mindestens eine der Fraktionen des katalytisch gecrackten Naphthaproduktes eine Fraktion mit einem unteren Siedepunkt im Bereich von 82,2°C bis 104,4°C und einem oberen Siedepunkt im Bereich von 204,4°C bis 221,1°C enthält.
4. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß mindestens eine andere Fraktion des katalytisch gecrackten Naphthaproduktes einen unteren Siedepunkt im Bereich von 121,1°C bis 193,3°C und einen oberen Siedepunkt im Bereich von 176,7°C bis 232,2°C besitzt.
5. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß eine Fraktion des katalytisch gecrackten Naphthaproduktes mit einem unteren Siedepunkt im Bereich von 121,1°C bis 193,3°C und einem oberen Siedepunkt im Bereich von 176,7°C bis 232,2°C in Stufe (c) nicht erneut gecrackt wird.
6. Verfahren nach jedem der Ansprüche 2 bis 5, dadurch gekennzeichnet, daß das in Stufe (d) erhaltene Produkt reformiert wird.
7. Verfahren nach jedem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der Olefingehalt des gecrackten Naphthaproduktes im Bereich von 20 bis 40 Gew. %, bezogen auf das Gewicht des Naphthaproduktes, liegt.
8. Verfahren nach jedem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Bedingungen der Wasserstoffbehandlung oder des Hydrofinierens in Stufe (d) innerhalb der folgenden Bereiche ausgewählt sind, so daß ein für die Zugabe zu einem Benzinmischpool geeignetes Produkt resultiert:

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|   | Verfahrensparameter                                   | Verfahrensbedingungen |
|---|---|-----------------------|
|   | Druck, kPa (Überdruck)                                | 413,7 bis 3447,5      |
|   | Temperatur, °C  | 204,4 bis 426,7       |
| 5 | Beschickungsgeschwindigkeit, LHSV ( $\text{h}^{-1}$ ) | 1 bis 80              |
|   | Wasserstoff/Naphtha-Verhältnis, liter/liter           | 35,62 bis 712,5       |

9. Verfahren nach jedem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Bedingungen der Wasserstoffbehandlung oder des Hydrofinierens in Stufe (d) in den folgenden Bereichen gewählt sind, so daß ein zum Reformieren über einem schwefelempfindlichen Edelmetallreformierkatalysator geeignetes Produkt resultiert:

|    | Verfahrensparameter                                   | Verfahrensbedingungen |
|----|---|-----------------------|
| 15 | Druck, kPa (Überdruck)                                | 689,5 bis 13790       |
|    | Temperatur, °C  | 204,4 bis 426,7       |
|    | Beschickungsgeschwindigkeit, LHSV ( $\text{h}^{-1}$ ) | 1 bis 25              |
| 20 | Wasserstoff/Naphtha-Verhältnis, liter/liter           | 35,62 bis 534,3       |

10. Verfahren nach jedem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß das in die erste Crackzone eingeleitete schwefelhaltige Kohlenwasserstoffeinsatzprodukt ein Gasöl ist, das unter 565,5°C siedet.

11. Verfahren nach jedem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß 80 bis 100% der Olefine im katalytisch gecrackten Naphthaeinsatzprodukt, das in die zweite Crackzone eingeleitet wird, in der zweiten Crackzone gesättigt werden.

12. Verfahren nach jedem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß das in die zweite Crackzone eingeleitete katalytisch gecrackte Naphthaeinsatzprodukt bei einer Temperatur im Bereich von 426 bis 593°C und einem Überdruck im Bereich von 0 bis 344,75 kPa umgesetzt wird.

13. Verfahren nach jedem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß das in die zweite Crackzone eingeleitete katalytisch gecrackte Naphthaeinsatzprodukt bei einer Temperatur im Bereich von 482,2 bis 554,4°C umgesetzt wird.

## Revendications

1. Procédé de production d'essence à indice d'octane élevé, comprenant les étapes suivantes, en combinaison:

(a) craquage d'une charge hydrocarbonée dans une première zone de craquage sur un premier catalyseur de craquage pour obtenir un produit naphta de craquage catalytique;

(b) extraction du produit naphta de craquage catalytique de la première zone de craquage;

(c) recraquage du produit naphta de craquage catalytique, ou d'une ou plusieurs fractions de ce produit, sans dilution avec d'autres hydrocarbures, sur un catalyseur du type zéolite à base d'aluminosilicate cristallin dans une deuxième zone de craquage, pour en saturer au moins une partie des oléfines qu'il contient, caractérisé en ce que la charge hydrocarbonée est une charge hydrocarbonée contenant du soufre et que le craquage catalytique de l'étape (a) donne un produit naphta ayant subi un craquage catalytique ayant une teneur en oléfines comprise entre 10 et 60% sur la base du poids du produit naphta et que, dans l'étape (c), le produit naphta, ou au moins l'une de ses fractions, est désulfuré et qu'au moins 50% des oléfines, sur la base du poids du produit naphta de craquage catalytique ou de sa fraction, sont saturés, et que le procédé comprend en outre l'étape (d) dans laquelle au moins une fraction du produit recraqué de l'étape (c) est hydrotraitée ou hydrofinée pour produire une essence ou un composant de mélange d'essence à indice d'octane élevé et à faible teneur en soufre.

2. Procédé selon la revendication 1, caractérisé en ce qu'au moins l'une des fractions du produit naphta de craquage catalytique comprend une fraction intermédiaire ayant un point d'ébullition initial compris entre 120°F (48,9°C) et 250°F (121,1°C) et un point d'ébullition final compris entre 250°F (121,1°C) et 380°F (193,3°C).

3. Procédé selon la revendication 1, caractérisé en ce qu'au moins l'une des fractions du produit naphta de craquage catalytique comprend une fraction ayant un point d'ébullition initial compris entre 180°F (82,2°C) et 220°F (104,4°C) et un point d'ébullition final compris entre 400°F (204,4°C) et 430°F (221,1°C).

4. Procédé selon la revendication 2, caractérisé en ce qu'au moins une autre fraction du produit naphta de craquage catalytique présente un point d'ébullition initial compris entre 250°F (121,1°C) et 380°F (193,3°C) et un point d'ébullition final compris entre 350°F (176,7°C) et 450°F (232,2°C).

5. Procédé selon la revendication 2, caractérisé en ce qu'une fraction du produit naphta de

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craquage catalytique, ayant un point d'ébullition initial compris entre 250°F (121,1°C) et 380°F (192,3°C) et un point d'ébullition final compris entre 350°F (176,7°C) et 450°F (232,2°C) n'est pas recraquée dans l'étape (c).

6. Procédé selon l'une quelconque des revendications 2 à 5, caractérisé en ce qu'il comprend l'étape supplémentaire consistant à reformer le produit obtenu dans l'étape (d).

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que la teneur du produit naphta craqué en oléfines est comprise entre 20 et 40% en poids sur la base du poids du produit naphta.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que les conditions d'hydrotraitement ou d'hydrofinage de l'étape (d) sont choisies de façon à donner un produit pouvant être ajouté à une formulation de mélange pour essence, dans les plages suivantes:

|    | Variable de procédé                            | Conditions de procédé      |
|----|--|----------------------------|
| 15 | Pression, kPa relatif (psig)                   | 413,7 à 3447,5 (60 à 500)  |
|    | Température, °C (°F)                           | 204,4 à 426,7 (400 à 800)  |
|    | Vitesse d'alimentation, VVH (h <sup>-1</sup> ) | 1 à 80                     |
|    | Débit hydrogène/naphta, litres/litre (SCF/B)   | 35,62 à 712,5 (200 à 4000) |

9. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que les conditions d'hydrotraitement et d'hydrofinage de l'étape (d) sont choisies de façon à donner un produit pouvant être utilisé en tant que charge pour être reformé sur un catalyseur de reformage à base de métaux nobles sensibles au soufre, dans les plages suivantes:

|    | Variable de procédé                          | Conditions du procédé      |
|----|--|----------------------------|
| 25 | Pression, kPa relatif (psig)                 | 689,5 à 13790 (100 à 2000) |
|    | Température, °C (°F)                         | 204,4 à 426,7 (400 à 800)  |
| 30 | Débit d'alimentation, VVH (h <sup>-1</sup> ) | 1 à 25                     |
|    | Débit hydrogène/naphta, litres/litre (SCF/B) | 35,62 à 534,3 (200 à 3000) |

10. Procédé selon l'une quelconque des revendications 1 à 9, caractérisé en ce que la charge hydrocarbonée contenant du soufre introduite dans la première zone de craquage est un gasoil bouillant en dessous de 1050°F (565,5°C).

11. Procédé selon l'une quelconque des revendications 1 à 10, caractérisé en ce que 80 à 100% des oléfines de la charge de naphta de craquage catalytique introduite dans la deuxième zone de craquage sont saturées pendant les réactions dans la deuxième zone de craquage.

12. Procédé selon l'une quelconque des revendications 1 à 11, caractérisé en ce que l'on fait réagir la charge de naphta de craquage catalytique introduite dans la deuxième zone de craquage à une température comprise entre 800°F (426°C) et 1100°F (593,3°C) et sous une pression comprise entre 0 et 344,75 kPa relatifs (entre 0 et 50 psig).

13. Procédé selon l'une quelconque des revendications 1 à 12, caractérisé en ce que l'on fait réagir la charge de naphta de craquage catalytique introduite dans la deuxième zone de craquage à une température comprise entre 900°F (482,2°C) et 10,30°F (554,4°C).